

# Intrinsic *DX* centers in ternary chalcopyrite semiconductors

*“Why metastable intrinsic defects cause open-circuit-voltage limitation and how they can be avoided”*

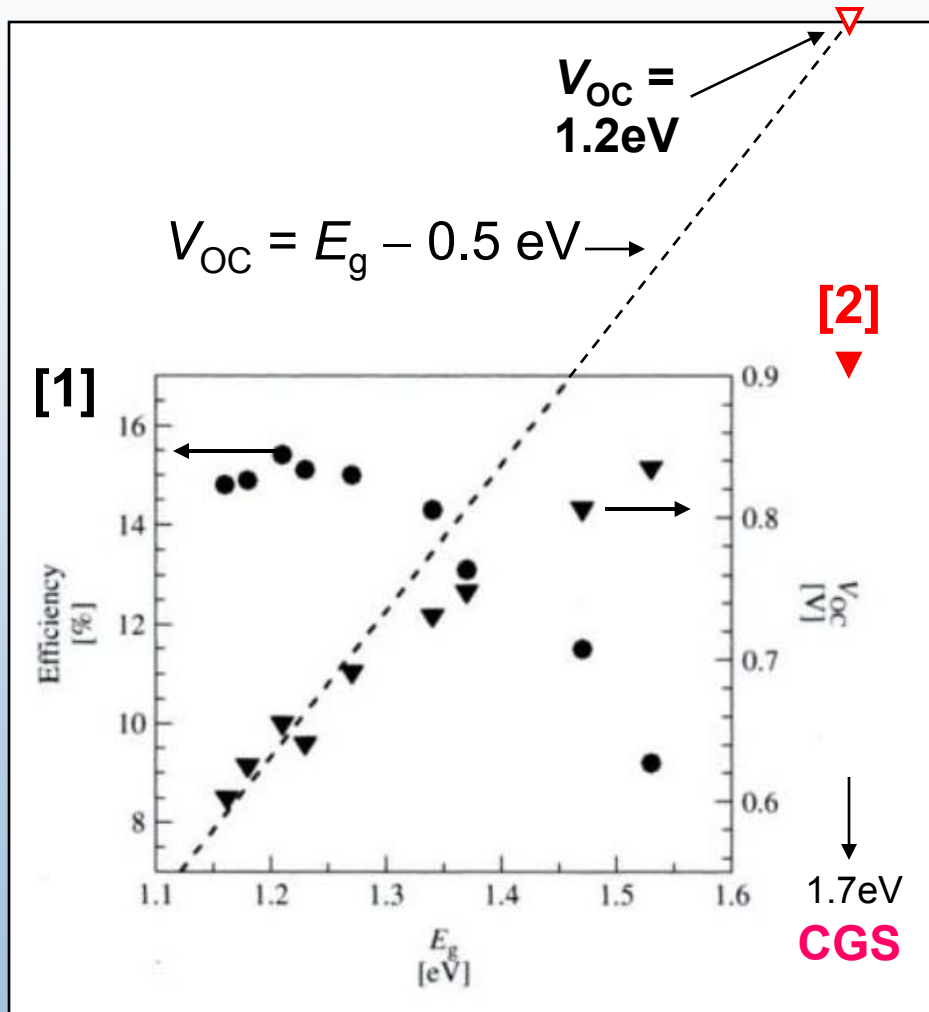
**Stephan Lany and Alex Zunger**

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# $V_{oc}$ saturation in CIGS

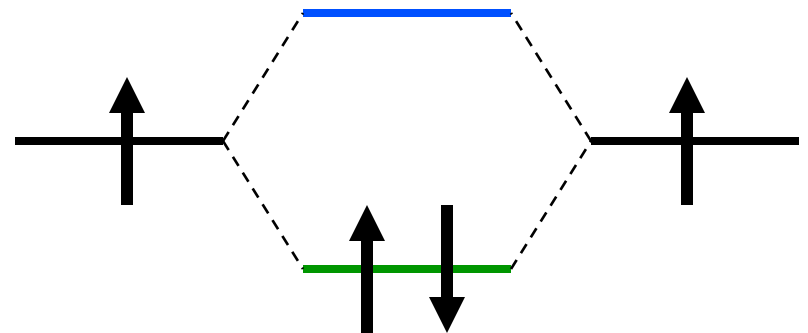
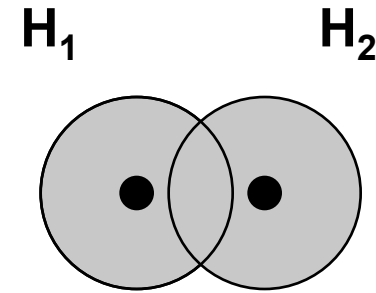
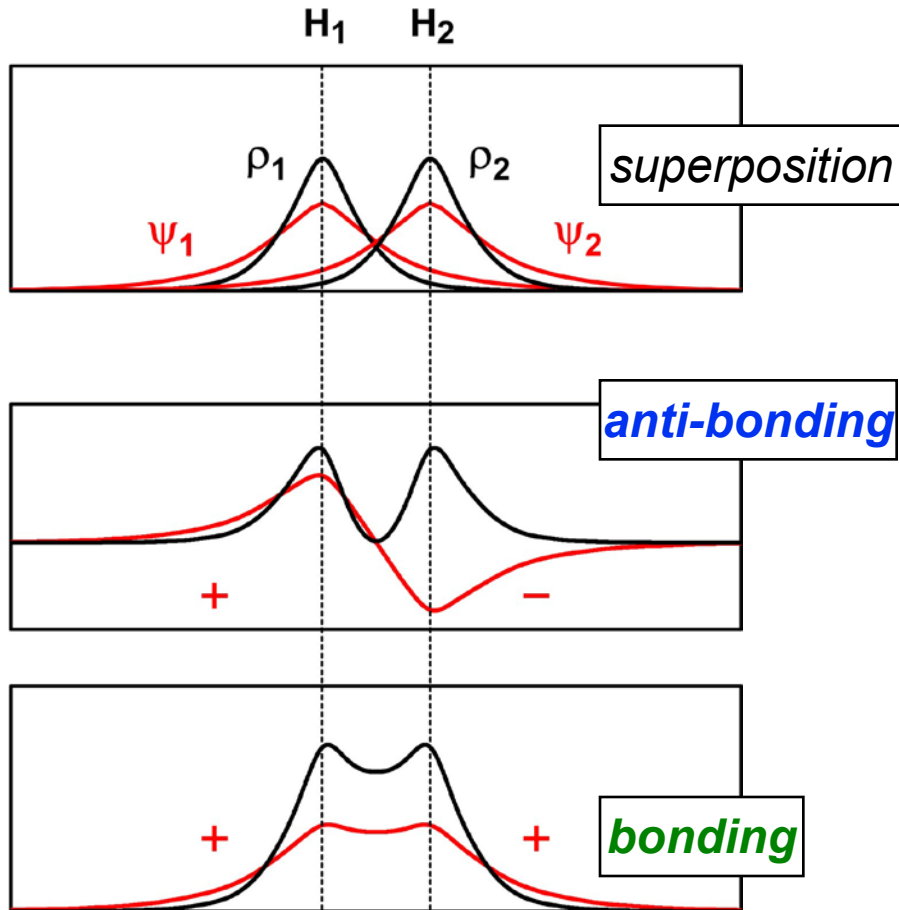


## Higher $V_{oc}$ :

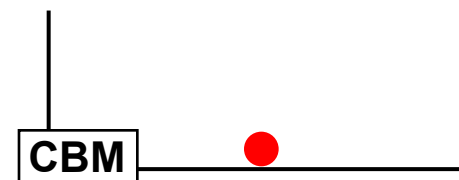
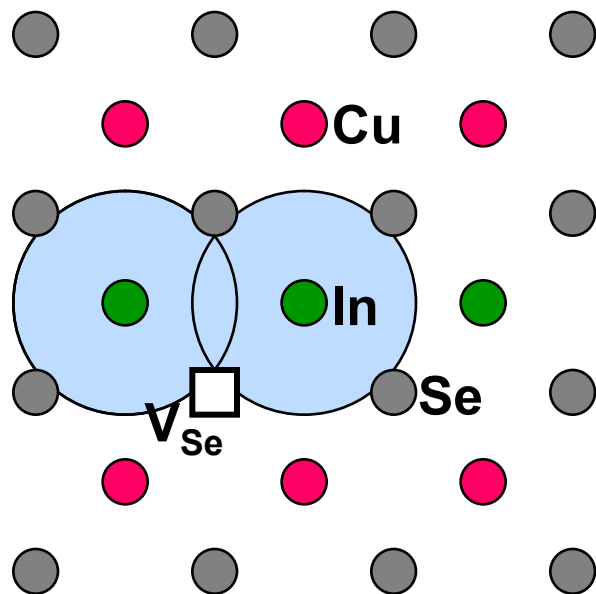
- Higher  $\eta$  for single-junction
- Needed for TF tandem
- Reason: Recombination due to deep defects [3]

- [1] W.N. Shafarman and L. Stolt, in: *Handbook of Photovoltaic Science and Engineering*
- [2] R. Kniese, M. Lammer, U. Rau, M. Powalla, TSF **451-452**, 430 (2004).
- [3] G. Hanna, A. Jasenek, U. Rau, H.W. Schock, TSF **387**, 71 (2001).

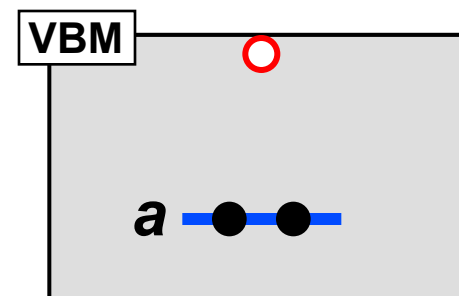
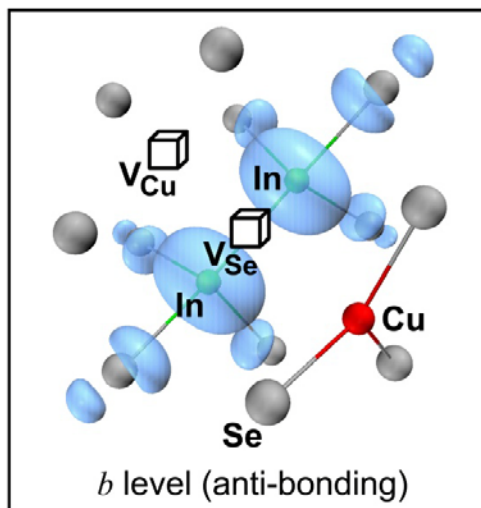
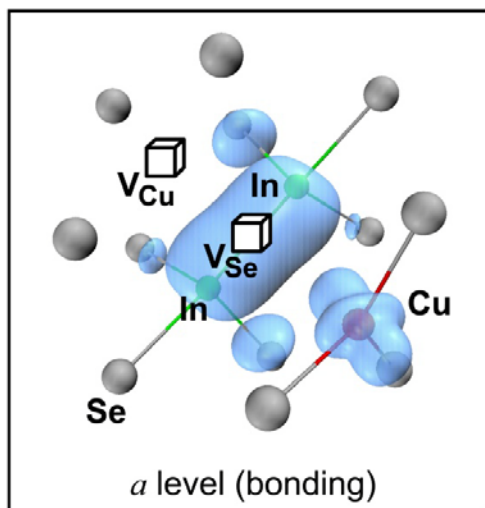
# Defects levels (I) – Example: Orbital interaction in the $H_2$ molecule



# Defects levels (II): Se-vacancy in $\text{CuInSe}_2$

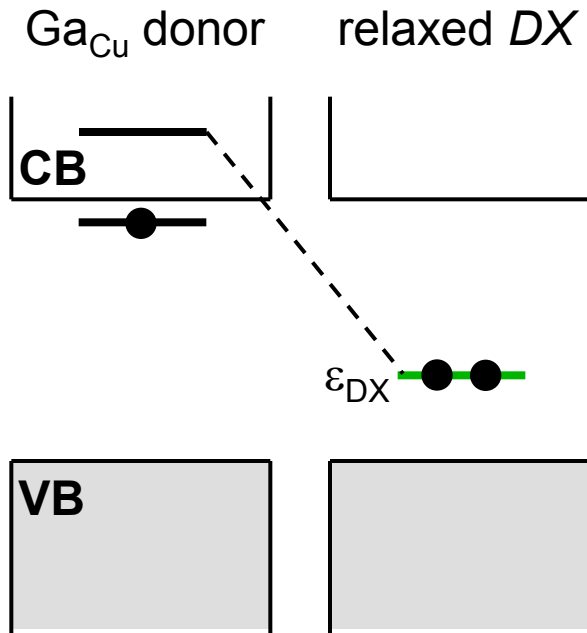


$b$  —



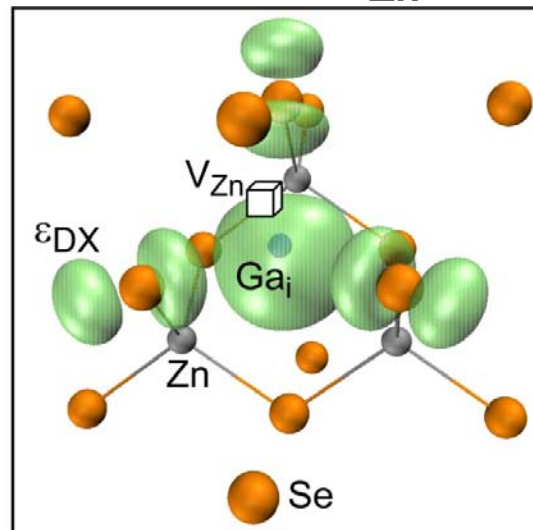
***Intrinsic DX* centers in ClGS**

# DX centers: *Electron traps formed due to lattice relaxations*



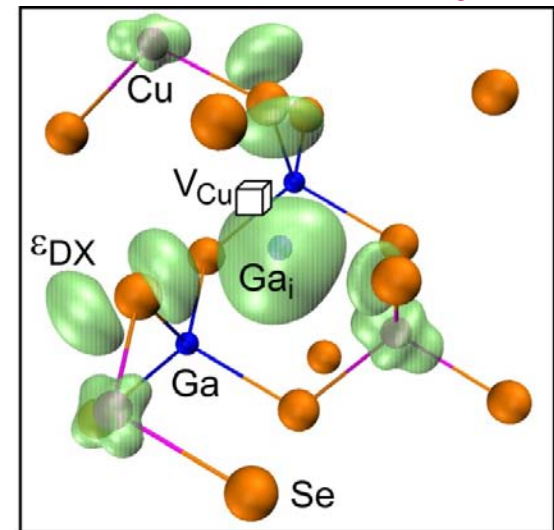
## **Extrinsic** DX in II-VI

ZnSe:Ga<sub>Zn</sub>



## **Intrinsic** DX in CIGS

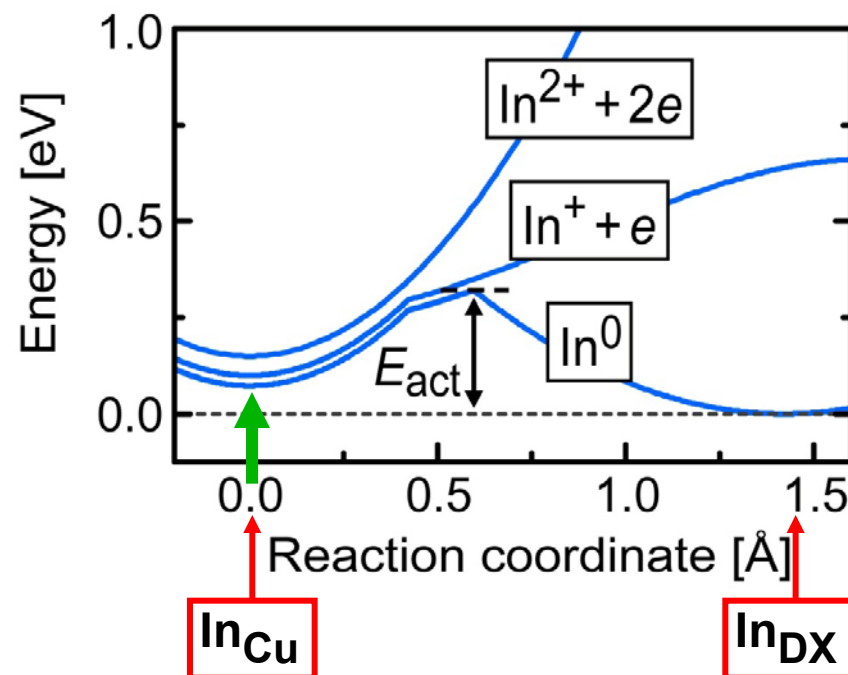
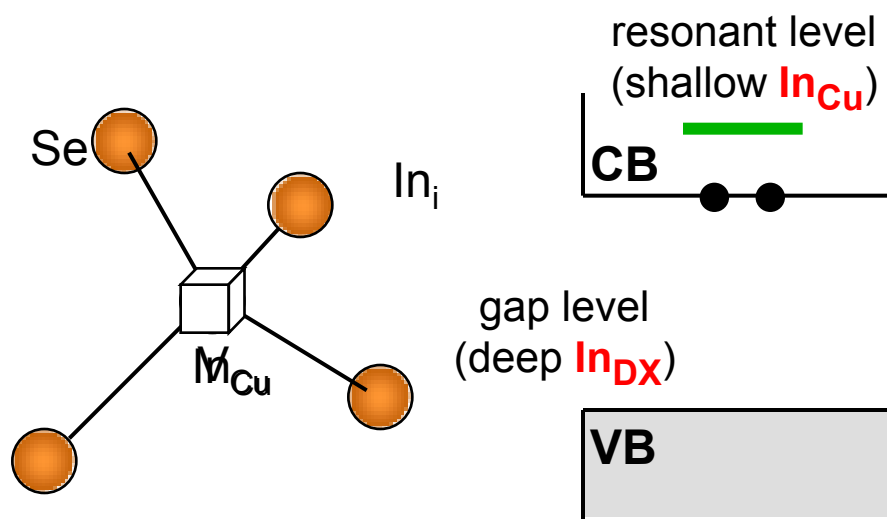
CuGaSe<sub>2</sub>:Ga<sub>Cu</sub>



In II-VI, DX centers require **extrinsic** impurities  
In CIGS, **native defects** (In<sub>Cu</sub>, Ga<sub>Cu</sub>) exhibit DX behavior

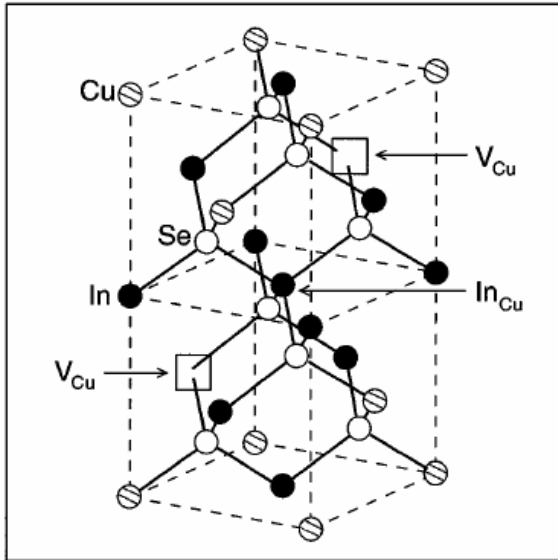
S. Lany and A. Zunger, Phys. Rev. Lett. **100**, 016401 (2008).

# Evolution of ionic structure, electron-level, and energy during the transition into the deep DX state



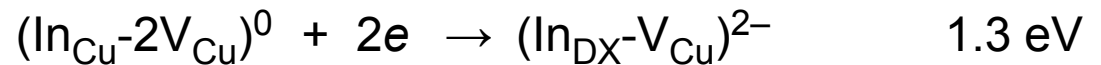
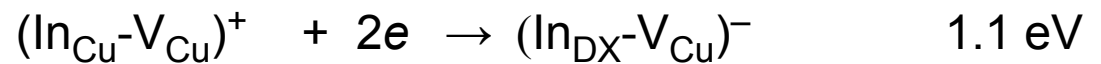
# Critical Fermi levels for electron-trapping

$\text{In}_{\text{Cu}}$  ( $\text{Ga}_{\text{Cu}}$ ) exists isolated or in complexes, e.g.,  $(\text{In}_{\text{Cu}}-2\text{V}_{\text{Cu}})$  [1]



Transition

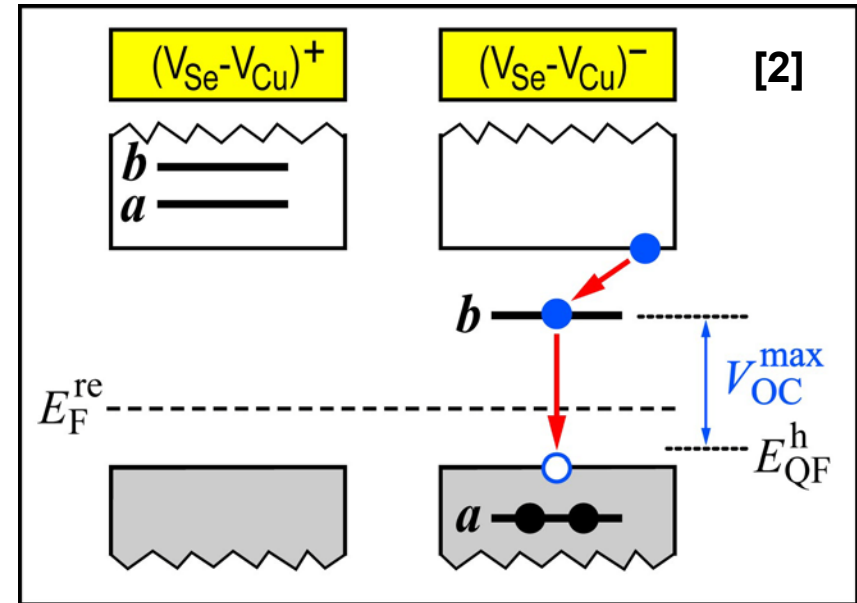
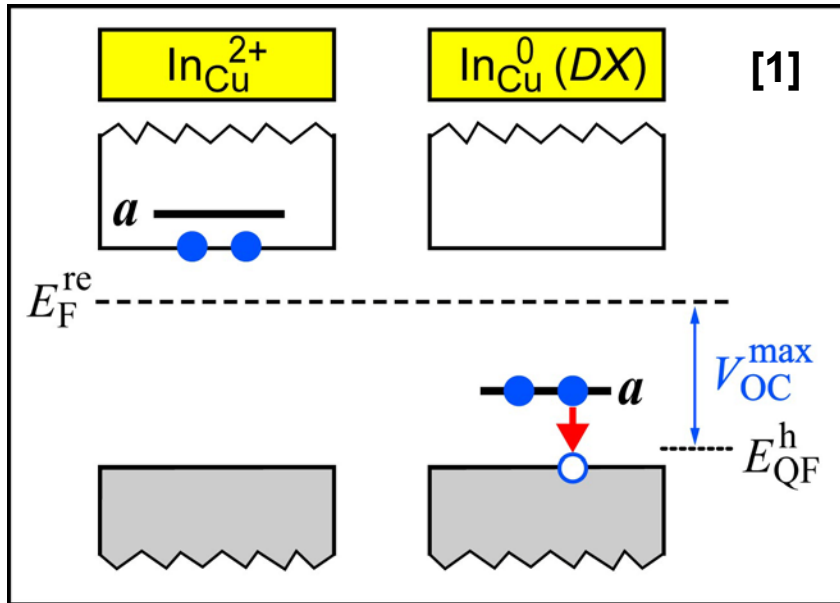
occurs  
above  
 $E_F > E_V +$



Electron-trapping due to DX centers occurs mainly in wider-gap  $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$  alloys with  $x \geq 0.3$



# $V_{OC}$ limitation by $In_{Cu}$ , $Ga_{Cu}$ , $V_{Se}$ and their complexes with $V_{Cu}$



$In_{Cu}$ ,  $Ga_{Cu}$ :  $V_{OC}$  is limited by the transition that causes atomic reconfiguration  
 $V_{Se}-V_{Cu}$ : The negative (acceptor) configuration exhibits deep trap level  
 Both types of defects limit  $V_{OC}$  below  $\sim 1$  eV

[1] S. Lany and A. Zunger, Phys. Rev. Lett. **100**, 016401 (2008).

[2] S. Lany and A. Zunger, J. Appl. Phys. **100**, 113725 (2006).

***How to avoid  $V_{OC}$  limiting  
metastable defects?***

# Formation energies vs growth conditions

$$\Delta H_{D,q}(\mu, E_F) = [E_{D,q} - E_{\text{host}}] + [\mu_{\text{host}} - \mu_D] + q \cdot E_F$$

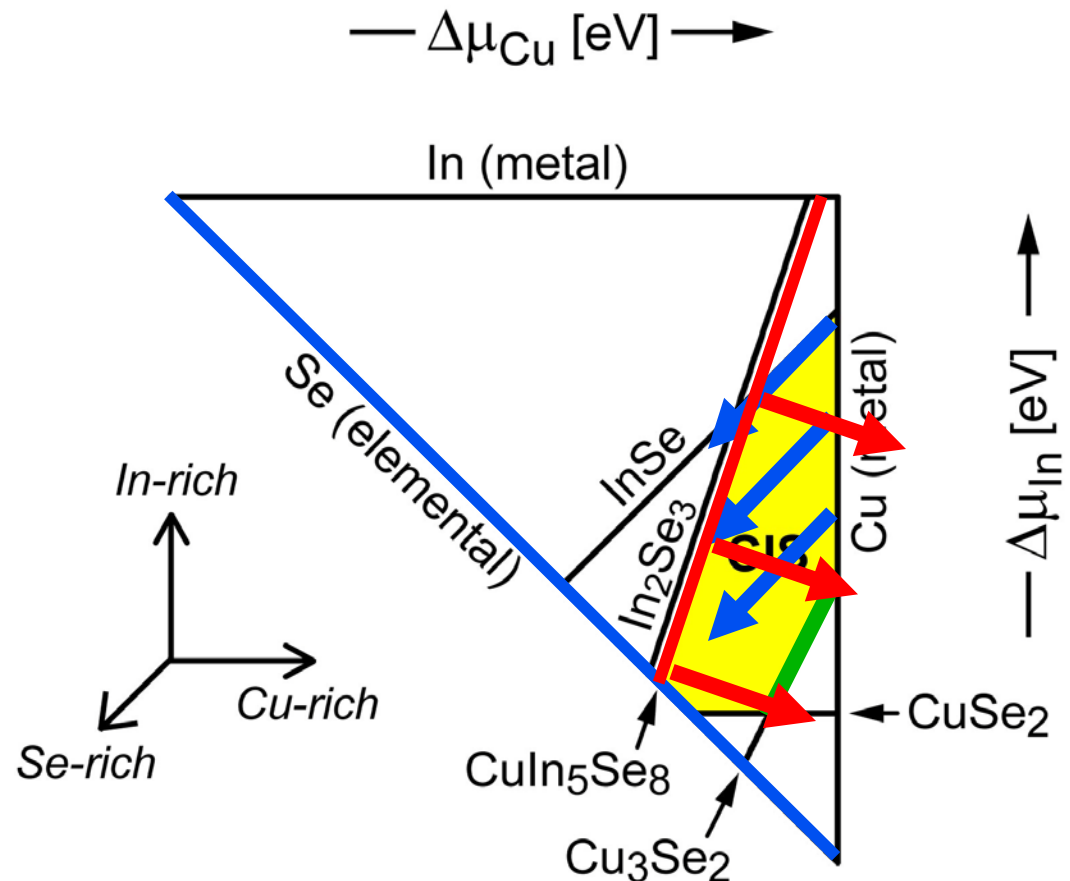
## CuInSe<sub>2</sub> stability condition

$$\Delta\mu_{\text{Cu}} + \Delta\mu_{\text{In}} + 2\Delta\mu_{\text{Se}} = \Delta H_f(\text{CIS})$$

## Competing phases

$$\text{e.g., } 3\Delta\mu_{\text{Cu}} + 2\Delta\mu_{\text{Se}} \leq \Delta H_f(\text{Cu}_3\text{Se}_2)$$

- Minimize  $\text{In}_{\text{Cu}}$ ,  $\text{Ga}_{\text{Cu}}$ ,  
( $\text{In}_{\text{Cu}} - 2V_{\text{Cu}}$ )
- Minimize  $V_{\text{Se}}$ , ( $V_{\text{Se}} - V_{\text{Cu}}$ )
- Cu-rich / Se-rich growth



## Trade-offs for minimizing $V_{oc}$ limiting defects

**Minimizing defects:**

Se-rich / Cu-rich

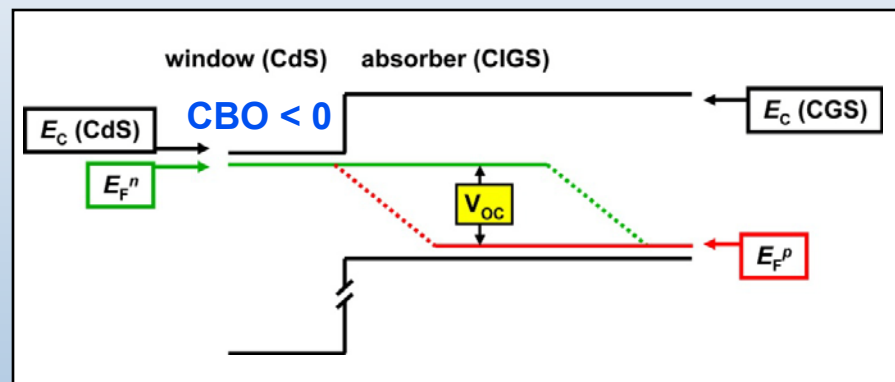
e.g., phase-equilibrium with  $\text{Cu}_3\text{Se}_2$

**Type inversion:**

Se-poor / III-rich (Cu-deficient) [1]

**Other causes of  $V_{oc}$  limit. :**

band-offset [2], ...?



[1] S. Lany *et al.*, Appl. Phys. Lett. **86**, 042109 (2005)

[2] M. Morkel *et al.*, Appl. Phys. Lett. **79**, 4482 (2001)

# Conclusions

- Intrinsic donor-type defects  $\text{In}_{\text{Cu}}$ ,  $\text{Ga}_{\text{Cu}}$ , and  $\text{V}_{\text{Se}}$ , and their complexes with  $\text{V}_{\text{Cu}}$  cause metastability, but also act to limit  $V_{\text{OC}}$
- Growth conditions which minimize these defects (Cu-rich/Se-rich) are very different from those currently used
- Overcoming  $V_{\text{OC}}$  limitation requires to address other issues and trade-offs

## ***References***

S. Lany and A. Zunger, Phys. Rev. Lett. **100**, 016401 (2008)  
S. Lany and A. Zunger, J. Appl. Phys. **100**, 113725 (2006)

***Stephan\_Lany@NREL.gov***